

XXII. *Remarks on the Extractive Material of Urine, and on the Excretion of Sulphur and Phosphorus by the Kidneys in an unoxidized state.* By EDMUND RONALDS, Ph.D., Giessen. Communicated by GOLDING BIRD, A.M., M.D., F.R.S., &c.

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SOME months back, at the instigation of Dr. GOLDING BIRD, I undertook some experiments to ascertain whether, in cases of diseased and imperfect function of the lungs or liver, when the normal quantity of carbon could not be discharged from the system by those channels, the kidneys undertook an extra duty, and whether under such circumstances an excess of carbon could be shown in the urine above that usually secreted under healthy conditions.

Should this question be answered in the affirmative, and should it be found that a larger amount of carbon was excreted by the urine in persons affected with such diseases, a practical application might reasonably be made of the fact. For by stimulating the kidneys to still greater exertion, the amount of work required of the lungs or of the liver could be lessened, and thus a better chance offered them of being restored to a healthy state.

The method proposed for solving this problem was, to precipitate the urine of different patients suffering from diseases of the kinds mentioned, with basic acetate of lead, keeping it slightly alkaline by the addition of a few drops of ammonia, then to ascertain the amount of organic matter contained in the precipitate, and in particular the amount of carbon, and lastly to compare these quantities with those obtained in a similar manner from the urine of healthy individuals.

In endeavouring to determine the amount of organic matter in the lead precipitate by burning, as likewise in determining the quantity of carbon by an elementary analysis of the same precipitate with oxide of copper, results were obtained which did not agree, and many difficulties arose which it is not necessary to state now, but which rendered it absolutely necessary to separate by some means the organic matter from the oxide of lead before submitting it to analysis, and even that we might obtain accurately its quantity. Whilst employed in seeking an accurate mode of separation, Dr. SCHERER's paper appeared on the extractive matters of urine\*, in which a successful mode of separation is described, and the question at issue answered. Dr. SCHERER finds that the extractive or colouring matter of the urine contains a larger quantity of carbon and hydrogen when obtained from persons in whom the normal function of the lungs, of the liver or of the skin is deranged, than when taken from

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healthy subjects, and that the same excess of carbon passes off by the urine when the diet is more than usually rich in that element. From his paper however it does not appear that the quantity of this extractive or colouring matter passed during a certain space of time has been ascertained, and it strikes me that he assumes the quantity of extractive to be the same in all kinds of urine; this I think requires to be proved before it can be positively affirmed that more carbon and hydrogen do pass off by the urine in such diseased conditions, as a larger quantity of less highly carbonized extractive matter might compensate for the excess of carbon in the more highly carbonized, supposing the latter to be in less quantity. The relative quantity of these matters, and likewise the relative quantities of urea in a certain amount of urine, must be accurately determined before the conclusion can be considered as absolutely proved.

Whilst engaged with the foregoing researches, it occurred to me that it might not be devoid of interest to the physiologist to know the amount of sulphur which was secreted by the kidneys in an unoxidized state. That urine does contain sulphur, not in combination as sulphate, is evident from the smell of sulphuretted hydrogen which, mixed with that of ammonia, is evolved from it whilst undergoing spontaneous decomposition, also from the blackening which white lead paint suffers when exposed to the gases arising from putrid urine, and likewise from the fact, that urine allowed to putrefy in a glass vessel containing oxide of lead as one of its constituents, permanently blackens the glass. To set the fact beyond doubt, two portions of urine, previously deprived of mucus by acetic acid and filtration, each consisting of four fluid ounces, were measured; the one simply evaporated and burnt, the other evaporated and afterwards deflagrated with nitre. Each portion was then dissolved in dilute nitric acid, leaving a minute insoluble residue, and the sulphuric acid precipitated by chloride of barium; the results were as follows:—

Four fluid oz., simply incinerated, gave grs. gr. $\text{BaO SO}_3 \ 2\cdot656 = \text{SO}_3 \ 0\cdot902$ $= \text{S} \ 0\cdot366.$	Four fluid oz., deflagrated with nitre, gave in grains $\text{BaO SO}_3 \ 5\cdot697 = \text{SO}_3 \ 1\cdot954$ $= \text{S} \ 0\cdot783.$
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The quantity of sulphur in four fluid ounces not excreted in the state of sulphate was therefore 0·417 grain. To ascertain the quantity of sulphur excreted by the urine in twenty-four hours in an unoxidized state, the whole quantity passed by three individuals during that time was collected on different days and measured; its specific gravity was taken, and after being filtered from mucus, two portions of each specimen were measured in a specific-gravity bottle containing 1000 grain measures; one portion was simply acidified with nitric acid, and the sulphuric acid precipitated by nitrate of barytes. The other portion was evaporated with nitre and deflagrated, and the fused mass treated with dilute nitric acid and nitrate of barytes. From the difference in the quantities of sulphate of barytes obtained, the amount of sulphur not in an oxidized state was ascertained. The results from five different experiments are shown by the following Table.

TABLE, showing the relative proportions of Sulphur free and combined with oxygen excreted by the kidneys in twenty-four hours.

Quantity of urine in 24 hours.	58 fluid-ounces.		41·5 fluid-ounces.		62·5 fluid-ounces.		56 fluid-ounces.		43·5 fluid-ounces.	
Specific gravity.	1·014.		1·019.		1·017.		1·022.		1·016.	
	In 1014 grs.	In 100 grs.	In 1019 grs.	In 100 grs.	In 1017 grs.	In 100 grs.	In 1022 grs.	In 100 grs.	In 1016 grs.	In 100 grs.
Sulphate of barytes from the acid existing in the urine...	3·1658	0·312	4·354	0·427	4·215	0·414	7·314	0·715	3·922	0·386
Sulphate of barytes precipitated after oxidation of the free sulphur.....	4·4784	0·441	5·744	0·563	5·559	0·546	8·447	0·826	5·158	0·507
Quantity of unoxidized sulphur.....	0·18	0·017	0·19	0·018	0·183	0·018	0·157	0·0153	0·168	0·0165
Free sulphur excreted in 24 hours .....	4·639		3·715		4·998		3·866		3·247	

It thus appears that from three to five grains of sulphur pass off daily by the urine in some other combination than as sulphuric acid, and that these three to five grains amount to about one-fourth of the whole quantity of sulphur excreted by the kidneys. With a view to ascertain what compound contained this sulphur in the urine, I have examined the precipitates produced in urine by neutral and basic acetate of lead, after the separation of the sulphates by baryta, and find that they only contain traces of sulphur. The colouring matter described by SCHERER, and obtained by the method he adopts, likewise contains only a trace; whereas the liquid containing the urea, generally considered free from all other organic matter, which remains on the separation of the precipitate by basic acetate of lead, contains nearly the whole of this excess of sulphur, but how combined I have not yet been able to ascertain. The determination of this question, which I propose to examine, may possibly lead to some interesting facts, and perhaps throw some light upon the question respecting the formation of cystic oxide.

From some preliminary experiments made for the purpose of ascertaining whether phosphorus was contained in urine in any other compound than as phosphate, the following results were obtained.

To the four ounces of urine employed for the preliminary determination of the sulphuric acid and sulphur in the former experiment, after the precipitation of the sulphuric acid by barytes, some more nitrate of barytes was added and then the whole carefully neutralized with ammonia. The following quantities were obtained:—

Phosphate of barytes obtained from the  $\text{PO}_5$  naturally contained in urine was

$\text{BaO PO}_5$  5·775 grains

= $\text{PO}_5$  1·834

=P 0·805;

Phosphate of barytes obtained from urine after deflagration with nitre was

$\text{BaO PO}_5$  6·532 grains

= $\text{PO}_5$  2·074

=P 0·910;

showing an excess of phosphorus over that contained as phosphate in the four ounces of urine to be 0·105 grain.

In another experiment, in which the same portions of urine were employed as at the fifth column of the foregoing Table, the following were the results:—

Phosphate of barytes obtained from the  $\text{PO}_5$   
naturally contained in 1016 grs. of urine.

$\text{BaO PO}_5$  3·135 grains

= $\text{PO}_5$  0·993

=P 0·435.

Phosphate of barytes obtained from 1016 grs.  
of urine after deflagrating with nitre.

$\text{BaO PO}_5$  5·313 grains

= $\text{PO}_5$  1·687

=P 0·740.

Therefore 0·305 grain of phosphorus was contained in the 1016 grains of urine in an unoxidized state, which, calculated for the whole amount of urine passed in twenty-four hours, would amount to 5·896 grains. In some other specimens of urine which I examined there was however no approach to this quantity of phosphorus in an unoxidized state, and as the mode of analysis employed in these preliminary experiments was not the most accurate, I intend to make the determination of the quantity of phosphorus the subject of further experiments.

The only opportunity I have had of examining urine in a diseased state, was a portion obtained from a patient suffering from diabetes mellitus. As might have been anticipated from the character of this disease, the amount of sulphur which the urine contained in an unoxidized state, was considerably greater (by one-fourth) than in healthy urine.

The diabetic urine had a specific gravity of 1046.

Of this urine 1046 grains, precipitated with nitrate of barytes, gave—

4·308 grains sulphate of barytes = 1·479 grain  $\text{SO}_3$

= 0·592 grain S.

After the precipitation of the sulphuric acid by baryta, the urine was evaporated down with nitric acid, mixed with nitre and deflagrated. An excess of nitrate of barytes having been used to precipitate the sulphuric acid, there remained on treating the fused mass with dilute nitric acid, an insoluble residue of sulphate of barytes, the sulphuric acid of which had been derived from the oxidation of the sulphur by the nitre; the sulphate of barytes amounted to

1·837 grain = 0·629 grain sulphuric acid

= 0·251 grain sulphur, or 0·024 per cent.,

whilst in healthy urine the sulphur in this state never exceeded 0·018 per cent.